It is even closer to an equilibrium curve observed by Browning and Emmett[4] for reaction 4 when the carbon is presumably amorphous and is formed by the decomposition of metallic carbides at low temperature. This latter curve is shown as curve 3 in Figure 2. The difference between the curves is so small that one might suspect that the real equilibrium measured is that of reaction 4 with the carbon in a slightly more active form than the β-graphite. Similar deviations are reported by Troesch[8] on carbon supported on Ni, and by Leitnaker[9] on a U–C system. Although the formation of MoC phases is reported by Tutiya,[10] by Clougherty, *et al.*,[11] and established on X-rays of samples of Mo carbided to 7.6% C by Browning and Emmett,[1] the true equilibrium for reaction 3 must still be in doubt because of the difficulty in separating it from complications by reaction 4. The equilibrium for reaction 1, however, is, we believe, accurately defined by curve 1, Figure 2.

Acknowledgment. This project was made possible through AEC Grant No. NYO-2008-6.

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Molecular Orbital Calculation on Some Group I, II, and III Methyl Compounds[1]

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Abstract: The methyl compounds of the group I, II, and III elements display some interesting variations in structure. Some of the compounds are electron deficient in the sense that they form polymeric species through the delocalization of one or more bonding pairs. Examples of the latter are $((CH_3)_3Al)_2$, $(CH_3Li)_4$, and $((CH_3)_2Be)_x$. By contrast other compounds such as $(CH_3)_3B$ and $(CH_3)_2Zn$ are monomers showing little or no tendency toward association. An attempt has been made to understand the bonding factors which are responsible for the variations in structure of the methyl compounds of lithium, beryllium, boron, and aluminum largely on the basis of charge-iterated extended Hückel molecular orbital calculations. CNDO–SCF calculations were also performed on CH_3Li and $(CH_3Li)_4$.

The methyl compounds of the group I, II, and III elements display some interesting variations in structure. Some of these compounds are electron deficient in the sense that they form polymeric species through the delocalization of one or more bonding pairs. Examples of the latter are the trimethylaluminum dimer,[2] the dimethylberyllium polymer,[3] and the methyllithium tetramer.[4] By contrast, other methyl compounds such as trimethylboron[5] and dimethylzinc[6] are monomers showing little or no tendency toward association.

In the present paper we report the results of semiempirical molecular orbital calculations on some of these molecules. Our basic objective was to understand the bonding fractors which are responsible for these variations in structure. We were also interested in the validity of the concept of hyperconjugation, particularly in the case of $(CH_3)_3B$[7] since it has been argued[8] that this effect should be enhanced in this molecule due to C^-–B^+ polarity of the σ bond. Previously, Rundle[9] has described a simplified MO treatment of $(CH_3)_6Al_2$ and indicated that the bridge bonding in this species can be described as a combination of tetrahedral orbitals from aluminum and carbon or equivalently as a "methylated double bond."

More recently extended Hückel calculations have been performed on this molecule[10a] and $(CH_3)_3B$.[10b] Rough estimates have been made[4] for the MO energies of the lithium–carbon skeleton of $(CH_3Li)_4$, and the hypothetical methyllithium dimer has been the subject of an LCAO–SCF treatment.[11]

Methods of Calculation

Two types of Hückel molecular orbital calculations were performed on the following molecules: CH_3Li, $(CH_3Li)_4$, $(CH_3)_2Be$, $(CH_3)_3B$, $(CH_3)_6B_2$, $(CH_3)_3Al$, and $(CH_3)_6Al_2$. In addition CNDO self-consistent field calculations were performed on CH_3Li and $(CH_3Li)_4$.

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(a) Extended Hückel Calculations. One-electron eigenvectors and eigenvalues were computed using the method of Hoffmann.[12] Slater atomic orbitals were used except for the hydrogen 1s orbital where an exponent of 1.1 was employed. For the aluminum 3d orbital the exponent of 0.333 results from the valence electronic configuration $3s^23d$. The atomic coordinates were calculated from the pertinent bond distances and bond angles when available.[13] The following valence-state ionization potentials (vsip)[14] were used for the diagonal elements of the H matrix (eV): $H_{ii} = -13.06$ (H 1s), -5.39 (Li 2s), -3.54 (Li 2p), -9.92 (Be 2s), -5.96 (Be 2p), -14.91 (B 2s), -8.42 (B 2p), -21.01 (C 2s), -11.27 (C 2p), -12.27 (Al 3s), -6.47 (Al 3p). We assumed a vsip of -2.00 eV for (Al 3d). The off-diagonal elements were evaluated by the Wolfsberg–Helmholtz approximation[15]

$$H_{uv} = 0.5K(H_{uu} + H_{vv})S_{uv}$$

with $K = 1.75$.

(b) Extended Hückel Calculation with Charge Iteration (Self-Consistent Charge Method). This method,[16] hereinafter referred to as the SCC method, allows iterative adjustment of the Coulomb integrals according to the equation

$$H_{uu} = H_{uu}{}^0 - KQ_u$$

Here H_{uu} and $H_{uu}{}^0$ are the Coulomb integrals for charged and neutral atoms, respectively, and K is a constant (2.0 eV). The Slater exponents were adjusted according to the equation

$$\mu_u = \mu_u{}^0 + 0.35Q_u/n^*$$

where μ_u and $\mu_u{}^0$ are the exponents on the charged and neutral atoms, respectively, and n^* is the effective principal quantum number. The diagonal elements of the H matrix were evaluated by the method of Cusachs.[17] The values employed were (eV) $H_{uu} = -13.06$ (H 1s), -4.95 (Li 2s), -3.45 (Li 2p), -9.55 (Be 2s), -5.65 (Be 2p), -14.75 (B 2s), -8.1 (B 2p), -20.30 (C 2s), -10.60 (C 2p), -11.90 (Al 3s), -6.26 (Al 3p), and -1.75 (Al 3d). The last value was assumed.

(c) Self-Consistent Field Calculations (SCF–CNDO Method). These calculations were performed using a program written in our laboratories by one of the authors (W. D. W.) and M. W. Taylor. The program is based on the approximate LCAO–SCF theory of Pople, Santry, and Segal[18] in which differential overlap is neglected. The first part of the procedure involves calculating an initial set of molecular orbital coefficients, C_{iu}, by an extended Hückel procedure in which the diagonal elements of the H matrix are replaced by "average" ionization potentials, and the off-diagonal elements by $\beta_A{}^0S_{uv}$. The following "average" ionization potentials were used (eV):[19] -13.06 (H 1s), -5.39 (Li 2s), -3.54 (Li 2p), -19.44 (C 2s), -10.67 (C 2p). The bonding parameter values (eV) of β^0 (H) = -9.0, β^0 (Li) = -9.0, and β^0 (C) = -21.0 were taken from ref 19. Here, as in the extended Hückel calculation, the overlap integrals were calculated by Roothaan's method.[20]

The next stage involves calculation of the charge-bond order matrix

$$P_{uv} = 2\sum_i^{\text{occ}} C_{iu}C_{iv}$$

The P_{uv} matrix is then used to form the Hartree–Fock matrix, F_{uv}, which is solved to give a new set of eigenvectors, C_{iu}. This procedure is repeated until self-consistency is reached with a tolerance of 0.001 on all C_{iu}. Output of the program includes the eigenvectors, C_{iu}, the corresponding eigenvalues, e_i, the charge-density–bond order matrix, P_{uv}, and a Mulliken overlap population analysis.[21]

Results and Discussion

(i) Methyllithium. The calculated atomic charges and overlap populations for the methyllithium monomer and tetramer are shown in Table I. When methyllithium polymerizes, the overlap population of the C–H bond remains essentially constant and the decrease of Li–C overlap population is compensated for by the lithium–lithium bonding in the Li_4 tetrahedron. The overlap population of any one carbon atom is the same to each of the three lithium atoms of the nearest triangular face. There is no bonding character between a carbon atom and the far lithium atom, *i.e.*, the one

Table I. Calculated Atomic Charges and Overlap Populations for the Methyllithium Monomer and Tetramer

Compound	Bond	SCC[a]	SCF[b]
CH_3Li	Li–C	0.370	0.482
	C–H	0.830	0.654
Total overlap pop./Li atom		0.37	0.482
$(CH_3Li)_4$	Li–Li	0.168	0.424
	Li–C	0.148	0.333
	Li–C′	−0.029	0.027
	C–H	0.846	0.629
Total overlap pop./Li atom		0.928	2.343

Compound	Atom	Atomic Charges SCC	SCF
CH_3Li	Li	+0.49	+0.53
	C	−0.30	−0.39
	H	−0.06	−0.05
$(CH_3Li)_4$	Li	+0.45	+0.04
	C	−0.29	−0.26
	H	−0.05	+0.07

[a] The overlap populations between atoms A and B are calculated from the standard Mulliken formula (ref 21). [b] Calculated according to the formula $\Sigma_u\Sigma_v S_{uv}P_{uv}$ where P_{uv} is the bond order (eq 4) and S_{uv} is the overlap integral (ref 20).

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(13) The data for $(CH_3Li)_4$ are taken from ref 4. The data for $(CH_3)_3B$ and $(CH_3)_6Al_2$ are taken from ref 5a and 2a, respectively. For the idealized methyllithium and dimethylberyllium monomers the following bond distances were assumed: Li–C = 2.28 Å and Be–C = 1.93 Å. For the hypothetical (D_{2h}) trimethylborane dimer it was assumed that B–C (bridge) = 1.70 Å and B–C (terminal) = 1.56 Å. For the idealized (D_{3h}) trimethylaluminum monomer the Al–C bond distance was assumed to be 2.00 Å. In all cases, the carbon atoms were assumed to be tetrahedral with C–H bond distances = 1.10 Å.

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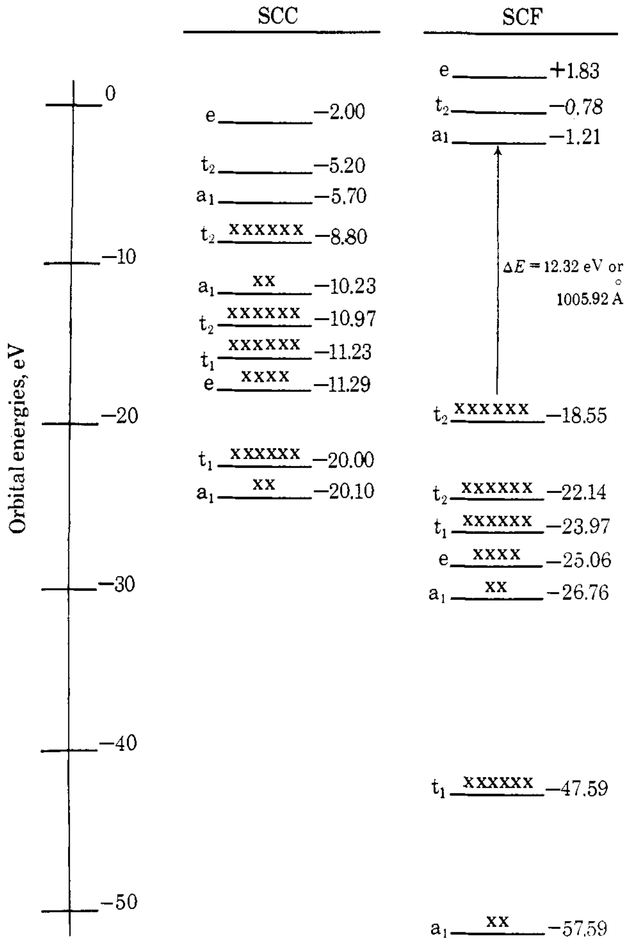

Figure 1. Twenty-two lowest lying molecular orbital for $(CH_3Li)_4$.

below each triangular face. This suggests that each CLi_3 unit is bonded by a delocalized four-center bond. The per cent 2s character in the carbon and lithium bonding orbitals is estimated to be 13 and 23%, respectively, on the basis of the equation of Van Der Voorn and Drago.[16] A significant feature of the overlap population data is the increase of the total overlap population per lithium atom when four CH_3Li units polymerize. Essentially this means that polymerization permits each lithium atom to enter into considerably more covalent bonding.

From Table II it can be seen that the three methods of calculation predict the methyllithium tetramer to be more stable than four isolated molecules of CH_3Li monomer. It should be emphasized, however, that this is not a reliable criterion of stability when one-electron methods are empolyed. This is due to the neglect of core repulsions and electron–electron interactions in the formulation of the Hückel total energy; *i.e.*, the total energy = $\Sigma_i^{occ} n_i e_i$, where n_i is the occupation number of the ith molecular orbital and e_i is the one-electron orbital energy. Consequently, the SCF data, which are based on a method which includes core and interelectronic repulsions, should be more reliable. However, the stability of the methyllithium tetramer is probably overemphasized (28.12 eV per CH_3Li unit). This probably results from the somewhat large bonding parameters (β^0) employed in the Pople, Santry, and Segal method.[18]

Table II. Total Energies for the Methyllithium Monomer and Tetramer (eV)

Compound	EHMO[a]	SCC[b]	SCF[c]
CH_3Li	−132.84	−102.04	−282.32
$(CH_3Li)_4$	−538.51	−412.34	−1241.75

[a] Extended Hückel molecular orbital method. [b] Extended Hückel method with charge iteration. [c] Self-consistent field method with complete neglect of differential overlap.

Fraenkel, Adams, and Williams[22] have suggested that alkyllithium species be regarded as lithium salts of carbanions. To some extent, our calculations substantiate this view since the carbon atoms of both the tetramer and the monomer are calculated to have negative charges by the extended Hückel method, the SCC method, and the CNDO-SCF method (Table I and Figure 2). However, it is important to point out that there is an appreciable positive overlap population between carbon and lithium in $(CH_3Li)_4$ (Table I) thus indicating covalency in this linkage. Further, from the SCC eigenvector and eigenvalue data, together with the Pople and Santry expression[23] for the contact term, we calculate the scalar coupling between Li^7 and C^{13} to be 0.77 Hz. Very recently[24] $J_{C^{13}-Li^7}$ has been found to be 14.5 Hz.

In Figure 1 are diagrammed the 22 lowest lying molecular orbitals of $(CH_3Li)_4$, the first 16 of which are occupied. It should be noted that the SCF transition energy includes Coulombic and exchange integrals, *i.e.*

$$^1\Delta E_{i\to j} = e_j - e_i - \left(\psi_j^2\left|\frac{e^2}{r_{12}}\right|\psi_i^2\right) + 2\left(\psi_j\psi_i\left|\frac{e^2}{r_{12}}\right|\psi_j\psi_i\right)$$

whereas in the SCC method the transition energy is simply the difference of orbital energies. The difference in the method of calculation is reflected in the widely different computed values for the parity-allowed $a_1 \leftarrow t_2$ transition. Thus the SCF method probably grossly overestimates the transition energy (12.32 eV or 1006 Å), while the independent electron model obviously underestimates the transition energy (3.1 eV or 4030 Å) since alkyllithium species do not absorb in the uv-visible region.[25]

(ii) Dimethylberyllium. The polymeric nature of this compound limited our calculations to the hypothetical $(CH_3)_2Be$ monomer. Assuming a linear geometry ($D_{\infty h}$) we calculate a carbon–beryllium overlap population of 0.67. As discussed in the next section, it is found that when the metal–carbon overlap population is less than ~0.8 the monomer appears to undergo polymerization. The carbon–beryllium bond is mainly σ in character since the overlap population for π bonding is only 0.060 per C–Be bond.

(iii) The Methyl Compounds of Boron and Aluminum. The overlap populations for $(CH_3)_3B$, $(CH_3)_6Al_2$, and the idealized molecules $(CH_3)_3Al$ and $(CH_3)_6B_2$ are shown in Table III.

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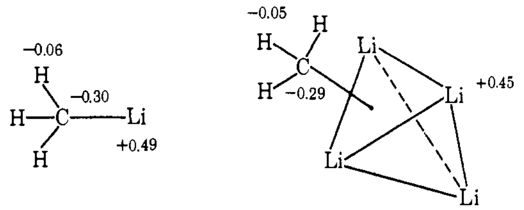

Figure 2. SCC atomic charges on CH_3Li and $(CH_3Li)_4$.

Carbon–boron π bonding (hyperconjugation) in trimethylborane was first proposed by Mulliken[7] to account for its existence as a monomer in contrast to trimethylaluminum. This general idea has since been quite widely accepted,[26] although there has been some criticism.[5b] In the present work it is found that, although there is some indication of a π-type interaction between the vacant $B(2p_z)$ orbital, and the occupied $C(2p_z)$ orbital, this is less than 10% of the σ bonding. More significant is the calculation on the hypothetical $(CH_3)_3Al$ monomer which indicates that the π-type interaction in this compound is almost the same as in $(CH_3)_3B$. Thus, hyperconjugation does not appear to account for the monomeric nature of $(CH_3)_3B$. An alternative explanation for the dimerization of $(CH_3)_3Al$ relates to the overlap population of the Al–C bond in the monomer (Table III). Both with and without Al(3d) orbitals in the basis set, this overlap population is less than 0.8. As mentioned in the section dealing with $(CH_3)_2Be$, metal–carbon overlap populations less than ~0.8 appear to result in polymerization. The value of 0.8 corresponds to the overlap population calculated for a carbon–hydrogen bond and appears to be an appropriate value for a normal covalent bond in systems of the type considered here. Increasing the coordination of aluminum *via* dimerization effects an increase in the total overlap population around each Al atom from 2.18 to 2.50 (or from 2.13 to 2.36 if Al(3d) orbitals are included in the basis set). This total overlap population comprises the sum of the nearest neighbor atomic populations and is thus a measure of *the increase of both σ and π bonding* upon dimerization.

Table III. Overlap Populations for Boron and Aluminum Methyl Compounds

Compound	Bond	Overlap population σ	π	Total
$(CH_3)_3B$	B–C	0.786	0.062	0.848
	C–H	0.808	...	0.808
$(CH_3)_6B_2$	B–C t[b]	0.826	−0.0007	0.825
	B–C b	...[a]	...[a]	0.420
	B–B	0.289	0.063	0.352
	C–H t	0.810	...	0.810
	C–H b	0.810	...	0.810
$(CH_3)_3Al$	Al–C	0.667	0.058	0.725
	C–H	0.790	...	0.790
$(CH_3)_6Al_2$	Al–C t	0.705	−0.005	0.704
	Al–C b	...[a]	...[a]	0.313
	Al–Al	0.412	0.056	0.468
	C–H t	0.800	...	0.800
	C–H b	0.790	...	0.790
$(CH_3)_3Al$[c]	Al–C	0.647	0.062	0.709
	C–H	0.790	...	0.790
$(CH_3)_6Al_2$[c]	Al–C t	0.720	0.006	0.730
	Al–C b	...[a]	...[a]	0.280
	Al–Al	0.359	−0.017	0.342
	C–H t	0.810	...	0.810
	C–H b	0.810	...	0.810

[a] A formal separation into σ and π bonding is not possible for these bonds. [b] t = terminal; b = bridge. [c] Al(3d) orbitals included in basis set.

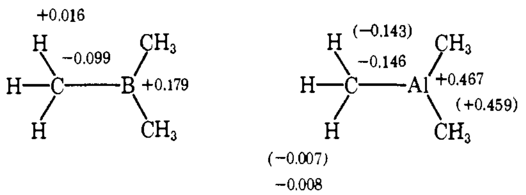

Figure 3. SCC atomic charges on $(CH_3)_3B$ and $(CH_3)_3Al$. Values in parentheses are for Al (3d) orbitals included in the basis set.

It has been suggested[2b] that, in addition to the factors described by Rundle,[9] the metal–metal bond may play an important role in regard to the question of dimerization of group III alkyls. The substantial overlap population for the Al–Al bond of $(CH_3)_6Al_2$ (Table III) is in accord with the idea of metal–metal bonding. Further, it would appear that this bond is as strong as the Al–C bridge bonds and is mainly σ in character since the π-overlap population is small (without Al(3d) orbitals) or slightly negative (with Al(3d) orbitals). However, our calculations also indicate that there is appreciable B–B bonding in the idealized dimer, $(CH_3)_6B_2$, as reflected by the B–B overlap population.

The total energies of $(CH_3)_3B$ and its hypothetical dimer (Table IV) indicate that the dimer is considerably less stable than two isolated molecules of $(CH_3)_3B$. However, the total energies of the trimethylaluminum dimer and two monomer units are very similiar by either type of calculation, and the dimer only becomes more stable when Al(3d) orbitals are included in the calculation. It is tempting to suggest that a contributing factor to the stability of the trimethylaluminum dimer is the availability of vacant d orbitals on aluminum. However, as pointed out earlier, it is not possible to draw such conclusions due to the neglect of core and interelectron repulsions in the extended Hückel method. Nevertheless, the experimental value[27] of 20.2 kcal/mole for the heat of dimerization of $(CH_3)_3Al$ indicates that there is probably only a small energy difference between the monomer and the dimer. Of course, the imponderable in calculations of this kind concerns simple steric effects. Vranka and Amma[2b] have shown that the methyl groups of $(CH_3)_6Al_2$ are quite tightly packed.

Table IV. Total Energies for Trimethylborane and Trimethylaluminum (eV)

	EHMO		SCC	
Compound	Without Al (3d) Orbitals	With Al (3d) Orbitals	Without Al (3d) Orbitals	With Al (3d) Orbitals
$(CH_3)_3B$	−410.6	...	−382.9	...
$((CH_3)_3B)_2$	−809.3	...	−759.6	...
$(CH_3)_3Al$	−405.5	−406.7	−365.7	−366.7
$((CH_3)_3Al)_2$	−810.0	−817.7	−731.2	−733.7

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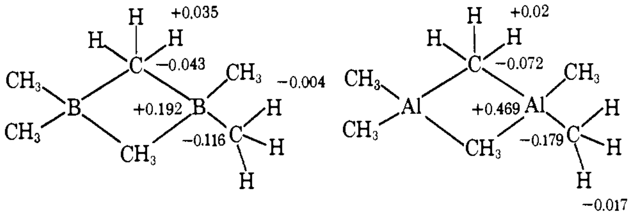
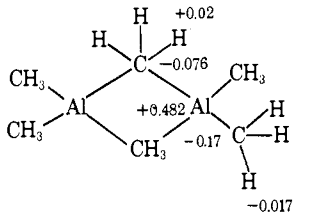
(26) See, for instance, F. G. A. Stone, *Chem. Rev.*, **58**, 101 (1958); and ref 8.

(27) A. W. Laubengayer and W. F. Gilliam, *J. Am. Chem. Soc.*, **63**, 477 (1941).



without 3d orbitals



with 3d orbitals

Figure 4. SCC atomic charges on $(CH_3)_6B_2$ and $(CH_3)_6Al_2$.

The reduction of the covalent radius from 1.26 (Al) to 0.88 Å (B) could therefore cause appreciable van der Waals repulsion forces between the methyl groups of $(CH_3)_6B_2$.

The calculated atomic charges for the group III methyl compounds are shown in Figures 3 and 4. The hydrogen atom charges of +0.016, −0.017, and +0.02 for $(CH_3)_3B$, and the terminal and bridge methyls of $(CH_3)_6Al_2$, respectively, correlate rather well with the observed[28-30] proton chemical shifts of τ 9.21, 9.69–9.7, and 10.59–10.8 for these positions. The calculated (SCC) hydrogen atomic charges of −0.05 for the methyllithium tetramer (Figure 2) also correlate well with the observed τ value of 11.3 for this compound.[22]

Another significant feature of the atomic charge data (Figures 3 and 4) concerns the substantially larger positive charge on Al in $(CH_3)_3Al$ than on B in $(CH_3)_3B$. It has been observed experimentally[31] that $(CH_3)_3Al$ is a stronger Lewis acid than $(CH_3)_3B$ toward $(CH_3)_3N$. This order has been rationalized previously[8] on the basis of strong B–CH_3 hyperconjugation and steric repulsion arguments. In view of our overlap population results, which indicate that hyperconjugation is approximately the same in $(CH_3)_3B$ as in $(CH_3)_3Al$, we suggest that the atomic charge of the central atom might play an important role in determining Lewis acidity.

Conclusions

An attempt has been made to understand the bonding factors which are responsible for the variations in structure of the methyl compounds of Li, Be, B, and Al on the basis of charge-iterated extended Hückel (SCC) calculations. CNDO-SCF calculations were also performed on CH_3Li and $(CH_3Li)_4$.

(i) The main reason for polymerization relates to the tendency of central atoms to achieve the maximum total overlap population. If the total overlap population per central atom is less than ~0.8, the system will tend to polymerize.

(ii) The π-type bonding (hyperconjugation) appears to be approximately the same for $(CH_3)_3B$ and $(CH_3)_3Al$ and less than 10% of the σ bonding. Thus, the reason that $(CH_3)_3Al$ dimerizes cannot be due to hyperconjugation effects.

(iii) Our calculations indicate that there are fairly strong metal-metal bonds in $(CH_3Li)_4$ and $(CH_3)_6Al_2$. The Al–Al bond is mainly σ in character.

Acknowledgment. The authors are grateful to the Robert A. Welch Foundation for financial support. We also thank Mr. James Hubka for assisting in the calculations involving the SCC program. The generous allotment of computer time by the University of Texas Computation Center is also appreciated. All calculations were performed on a CDC 6600 computer.

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